REMOVAL OF ZINC IONS FROM AQUEOUS SOLUTIONS BY SORPTIVE-FLOTATION USING LIMESTONE AS A LOWCOST SORBENT AND OLEIC ACID AS A SURFACTANT

S. E. GHAZY[†] and A. H. RAGAB[‡]

† *Chemistry Department, Faculty of Science, Mansoura University, P.O. Box 66, Mansoura, Egypt. ghazyse@mans.edu.eg; shabaneghazy@yahoo.com*
‡ *New Mansoura Water Treatment Plant, Mansoura City, Egypt. Fidodido_ahr@yahoo.com*

Abstract*— Environmental pollution, mainly in the aquatic systems, due to developments in industry, is one of the most significant problems of this century. Many industrial wastewater streams (ca. the metal working, semiconductor, and copper industries, mine water, etc.) contain heavy metals, which are of great environmental concern and must be removed prior to water discharge or water recycling. The present study aims to develop a simple, rapid and economic procedure for Zn^{2+} ions removal under the optimum conditions. It is based on the sorption of Zn^{2+} ions from aqueous solutions onto limestone fines (LS), which is an inexpensive and widespread over the globe, followed by flotation with oleic acid (HOL) surfactant. The different parameters (namely: solution pH, sorbent, surfactant and zinc concentrations, shaking times, ionic strength, temperature and the presence of foreign ions) influencing the sorptive-flotation process were examined. About 100 % of Zn^{2+} ions were removed from aqueous solutions at pH 7 after shaking for 5 min and at room temperature (~25ºC). The procedure was successfully applied to recover almost Zn^{2+} ions spiked to some natural water samples. A mechanism for sorption -flotation is suggested.

***Keywords*— zinc, sorptive-flotation, limestone, low-cost sorbent, oleic acid**

I. INTRODUCTION

Mobilization of heavy metals in the environment due to industrial activities is of serious concern due to their toxicity for humans and other life organisms. Removal of toxic heavy metals from industrial waste waters is essential to control environmental pollution (Puranike and Pakniker, 1999; Guangy and Thiruvenkatachari, 2003). At least 20 metals are classified as toxic and half of these are emitted into the environment in a quantity that poses risks to human health (Nasir *et al.,* 2007). The ability of water body to support aquatic life as well as its suitability for other uses, however, depends on trace elements.

Zn is used principally for galvanizing iron and more than 50% of metallic zinc goes into galvanizing steel, but is also important in the preparation of certain alloys. It is used for the negative plates in some electric batteries and for roofing and gutters in building constructions. Zinc is the primary metal used in making American pennies and is used in die casting in the automobile industry. Its oxide is used as a white pigment in water colors or paints, and as an activator in the rubber industry. Zinc metal is included in most single tablet and it is believed to possess anti-oxidant properties, which protect against premature aging of the skin and muscles of the body.

Trace concentration of zinc are important for the physiological functions of living tissues and regulate many other biochemical processes. However, just like other heavy metals, when Zn is discharged into natural waters at increased concentration in sewage, industrial waste water or from mining operations it can have severe toxicological effects on humans and aquatic ecosystem (Kortonekamp *et al.,* 1966).

The free zinc ion is a powerful Lewis acid up to the point of being corrosive. Stomach acid contains hydrochloric acid, in which metallic zinc dissolves readily to give corrosive zinc chloride. Hence, it is essential to remove Zn from industrial waste waters before transport and cycling into the natural environment.

Many technologies that could eliminate and/or reduce the presence of heavy metals in industrial effluents have been developed. These include precipitation and co-agulation, cementation, membrane separation, solvent extraction, ion-exchange, adsorption and bio-sorption (Palterson, 1989; Ghazy *et al.,* 2005). Flotation as a solid/liquid or liquid/liquid (or both) separation process has recently received a considerable interest owing to: simplicity, rapidity, economic, good separation yields (R > 95%) for small impurity concentrations (10^{-6}-10^{-2} mol/L), a large possibility of application for species having different nature and structure, flexibility and friability of equipment and processing for recovery purpose (Stoica *et al.,* 1998; Ghazy *et al.,* 2003). It is believed that this process will be soon incorporated as a clean technology to treat water and wastewater (Rubio *et al.,* 2002). For the aforementioned reasons a combination of adsorption and flotation into unified operation termed sportive-flotation could be considered as a vital process.

In recent years there has been a considerable interest in the development of new products which are abundant in nature, low in cost and have minimal environmental impact for restoration or remediation of natural resources (Gomez del-Rio *et al.,* 2004). Limestone (LS), which is produced in large quantities in many countries (among them is Egypt), is a low-cost reactive medium that can be used for the subsequent clean up of industrial effluents, leachates and contaminated ground water (Gomez del-Rio *et al.,* 2004; Komnitsas *et al.,* 2004; Bailey *et al.,* 1999). Hence, the present work aims to establish a rapid and simple sorptive-flotation procedure using LS (which is naturally occurring or readily available and alterative to existing commercial adsorbents) as a sorbent and oleic acid as a surfactant for removing zinc from aqueous solution and natural waters under the recommended conditions.

II. MATERIALS AND METHODS

A. Samples and Reagents Employed

The Limestone (LS), CaCO3, samples used in this study were obtained from the Al-Mokattam area in Cairo (Egypt) where some private and governorate quarries are located. The samples were crushed and pulverized in the laboratory and those with a mean size of ca. 12.5 µm were used in the experiments. The sample contained 92% calcite (CaCO3) and 3% dolomite (MgCO3), as found by chemical analysis (Ghazy *et al.,* 2001), with the reminder being composed of common minor constituents such as silica, clays, feldspar, pyrite, and sedrite (Bates and Jackson, 1980). The samples were dried for 2 h in an oven at 125ºC, packed into stopper bottles and stored in desiccators for future use. Functional groups of LS were characterized through infrared analysis. The LS spectrum coincided with pure CaCO3. The surface area and porosity of LS was measured using Brunauer, Emmett, Teller (BET) method. LS presented no BET porosity and its measured surface area was $3.88 m^2/g$. The pH values of points of zero charge (pH PZC) were 9.1 (not aged), 6.2 (aged 60 min) and 8.3 (aged several days) and this agreed with the previously reported data (Somasundran and Ager, 1967).

All the solutions were prepared from certified reagent grad chemicals. A zinc sulfate heptahydrate ($ZnSO_4.7H_2O$) stock solution was prepared and the working solutions were made by diluting the former with doubly distilled water. An oleic acid (HOL) stock solution, 6.36×10^{-2} mol/L, was prepared from food grade with sp. gr. 0.895 (provided by J.T. Baker Chemical Co.) by dispersing 20 mL of HOL in 1 L kerosene. Aqueous solutions of HNO_3 and NaOH were used for pH adjustments.

B. Apparatus

A Pekin-Elmer 2380 Atomic Absorption Spectrophotometer with air-acetylene flame was used for the determination of zinc concentration at 213.9 nm. The infrared analyses were undertaken via a Mattson 5000 FT-IR spectrophotometer using KBr disc method. The pH was measured using Jeanway 3311 pH meter, England. The stirring of the solutions was performed with a magnetic stirrer Model VEHP, Scientifica, Italy. The flotation procedure was carried out in a flotation cell, which was a cylindrical tube of 1.5 cm inner diameter and 29 cm length fitted with a stopcock at the bottom and a stopper at the top (Ghazy, 1995)

C. Procedure

To study the various parameters affecting the sorptive-flotation process, a 20 mL aliquot of a suspension containing 6.5 mg/L Zn^{2+} ions and 1000 mg/L sorbent (LS) of initial pH 5 was introduced into the flotation cell. The cell was shaken for 5 min (optimized time) to ensure complete adsorption of Zn^{2+} ions by LS. Then 3 mL of 1×10^{-3} mol/L HOL was added. The cell was again inverted 20 times by hand and allowed to stand for 5 min to complete flotation.

The residual Zn^{2+} ions concentration in the mother liquor was analyzed using a Perkin-Elmer 2380 atomic absorption spectrophotometer at a wavelength of 213.9 nm. The floatability percentage of Zn^{2+} ions (%F) was calculated from the relationship:

$$\%F = (C_i – C_r) / C_i \times 100, \qquad (1)$$

where C_i and C_r denote the initial and residual Zn^{2+} ions concentrations.

To study the flotation of LS alone, the previous procedural steps were conducted in the absence of Zn^{2+} ions. After complete flotation, the LS-containing float was filtered through a G5 sintered-glass filter (porosity, 1-1.5 µm) and dried to constant weight in an oven at 125ºC. The floatability percentage of LS (%F), was calculated from:

$$\%F = C_f / C_i \times 100, \qquad (2)$$

where C_i and C_f denote the initial and float concentrations of the LS sorbent. All experiments were carried out at room temperature (~ 25 ºC).

To asses the applicability of the procedure, another series of experiments were conducted on 1 L suspension of natural water samples (placed in a 2 L glass beaker) containing 5.0 or 8.0 mg of Zn^{2+} ions, 1000 mg/L of LS and 10 ml of 1×10^{-3} mol/L of HOL with an initial pH of 7. The suspension was stirred magnetically for 10 min at 250 rpm where it was noted that the Zn-LS-HOL system was self-floatable without a stream of air bubbles being necessary.

III. RESULT AND DISCUSSION

A. Floatability of Powdered Limestone

A preliminary series of experiments (using a constant concentration of HOL equal to 1×10^{-3} mol/L at pH 7) was undertaken in order to float various concentrations of LS. The results obtained are depicted in Fig. 1, from which it is clear that a maximum flotation (~100 %) for LS was attained over a wide concentration range up to 4000 mg/L. Hence, the concentration of powdered limestone favorable for Zn^{2+} ions removal was presumed to be 1000 mg/L.

Another series of experiments were conducted to study the effect of pH on the flotation of 1000 mg/L of LS using 1×10^{-3} mol/L HOL. The results are depicted in Fig. 2 and show that maximum flotation of LS (~100 %) was attained over the pH range 4-10. It should also be noted that at pH values less than 2, the process was not effective due to the partial dissolution of the LS sorbent. For this reason, a pH value of 7 was employed in all subsequent measurements.

To find out the suitable concentration of HOL for the complete flotation of 1000 mg/L of LS, a series of experiments were performed using different concentrations of HOL in acidic, neutral and alkaline media. The results shown in Fig. 3 indicate that the floatability of LS did not exceed 85 % at pH 3, but attained a maximum value (~100%) in the HOL concentration ranges of 10^{-4}-10^{-2} mol/L and 10^{-5}– 10^{-2} mol/L at pH values of 7 and 9, respectively. For simplicity, 1×10^{-3} mol/L HOL was used in other experiments at an initial pH of 7.

B. Floatability of Zn^{2+} Ions .

Effect of pH

Generally, adsorption and flotation are sensitive to variations in the pH of the medium and knowledge of how the pH value affects each system was a prerequisite to study sorptive-flotation method (Ghazy *et al.,* 2001). From the speciation diagram reported by Bradl (2004), using the reactions and equilibrium constants, it was concluded that at acidic pH < 7, the predominant ionic species are Zn^{2+} ions, whereas, zinc is present mainly as $Zn(OH)^+$ and $Zn(OH)_2$ near pH 9. By increasing the pH more than 9, the negative species $Zn(OH)_3^-$ and $Zn(OH)_4^{2-}$ appear (Baes and Messmer, 1976)..

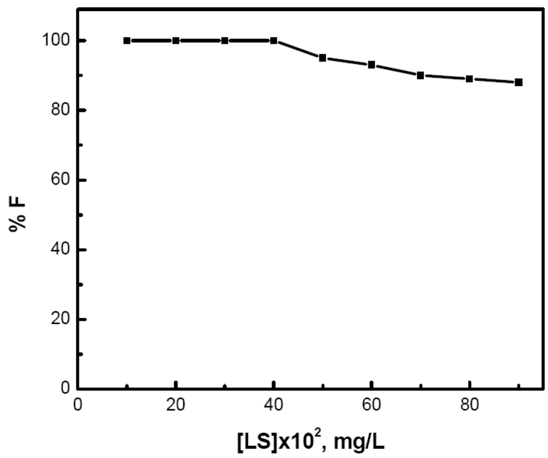

Figure 1. Floatability of different concentrations of LS using 1×10^{-3} mol/L HOL at pH 7.

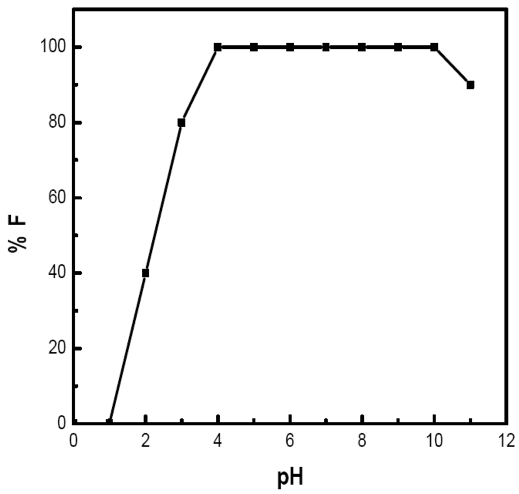

Figure 2. Floatability of 1000 mg/L of LS at different pH values using 1×10^{-3} mol/L HOL

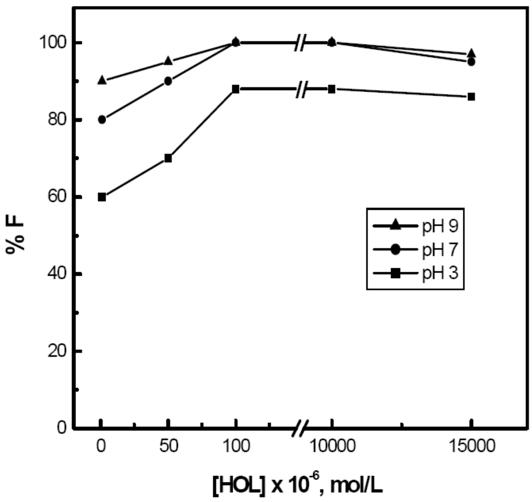

Figure 3. Floatability of 1000 mg/Lof LS at different concentrations of HOL using different pH values

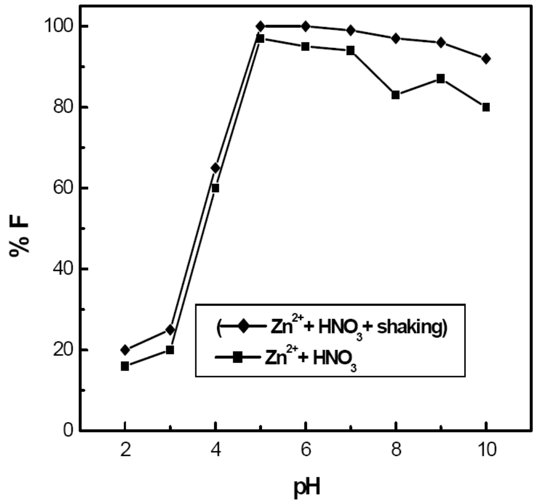

Figure 4. Floatability of 6.5 mg/L of Zn^{2+} ions at different pH values with or without shaking for 5 min using 1000 mg/L of LS and 1×10^{-3} mol/L of HOL

The influence of pH on the combined process (sorption and flotation) for the removal of 6.5 mg/L of Zn^{2+} ions was investigated in the presence of 1000 mg/L of LS using 1×10^{-3} mol/L of HOL with or without shaking for 5 min (Fig. 4). The pH of solutions was adjusted with HNO_3. At low pH values less than 3, the floatability is small due to the solubility of the LS (consists mainly from $CaCO_3$ and $MgCO_3$) at acidic medium; thereby hindering the sorption of Zn^{2+} ions. Around pH 5, the floatability increases to a maximum (~99 %) but with shaking for 5 min only, the flotation increase to about ~100 %, which maybe due to a good aggregation of the metal ions on the LS surface according to ion-exchange mechanism between Zn^{2+} ions and calcium containing LS in a similar manner to that reported (Mandjiny *et al.,* 1995). Moreover, Zn^{2+} ions may be adsorbed electrostatically with the negatively charged surface of limestone (Ghazy *et al.,* 2001). Therefore, pH 7 was recommended throughout all experiments.

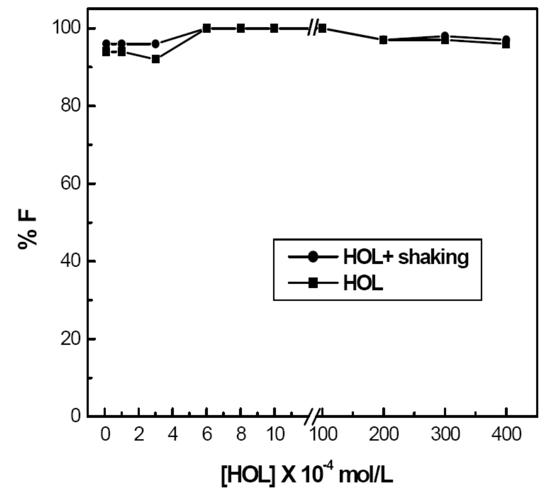

Figure 5. Floatability of 6.5 mg/L $Zn2^{+}$ ions using different concentrations of HOL at pH 7 with and without shaking

Effect of Surfactant Concentration

In order to find the suitable concentration of HOL for removing 6.5 mg/L of Zn^{2+} ions from aqueous solutions, a series of experiments were conducted at pH 7 in the presence of 1000 mg/L LS using different concentrations of HOL. The results obtained are presented in Fig. 5. It can be seen that the removal of Zn^{2+} ions attained ~95%. An enhancement in the flotation efficiency of Zn^{2+} ions to ~ 100% was achieved after shaking for 5 min. These maximal values were attained over the HOL concentration range of 5.0×10^{-4}-2×10^{-2} mol/L.

Higher concentrations of the surfactant impaired flotation. This impairment has been discussed by some workers (Ghazy *et al.,* 2001), who concluded that poor flotation at high surfactant concentration was caused by the formation of stable, hydrated envelope of surfactant on air bubbles surface or, perhaps, by the formation of a hydrated micelle coating on the solid surface. As a result, the hydrophobocity of the resulting surface was not satisfactory for flotation. Consequently, the concentration of HOL employed was fixed at 1×10^{-3} mol/L throughout all other studies.

Effect of Sorbent and Metal Ion Concentrations

Two parallel series of experiments were conducted to study the influence of powdered limestone concentration (Fig. 6) and changing the zinc ion concentration (Fig.7) on the removal percentage of Zn^{2+} ions from aqueous solutions at pH 7 using 1×10^{-3} mol/L of HOL without or with shaking for 5 min. As can be seen from Fig. 6, the removal percentage of Zn^{2+} ions increased as the LS dose increased, while it decreased as the concentration of the metal ion increased Fig. 7. The reason for attaining a maximum removal of Zn^{2+} ions (~ 100 %) at higher LS dose, after shaking for 5 min may be due to an increase in the number of binding sites on the sorbent available to Zn^{2+} ions. Hence, 1000 mg/L of LS may be a suitable dose for the removal of Zn^{2+} ions having a concentration of 6 mg/L after shaking for 5 min.

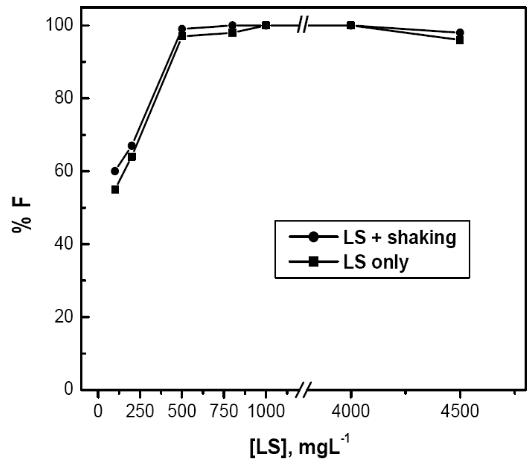

Figure 6. Floatability of 6.5 mg/L Zn^{+2} ions versus LS concentrations at pH 7 using 1×10^{-3} mol/L of HOL

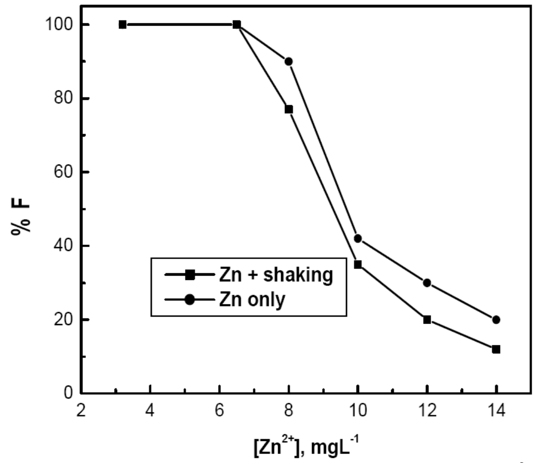

Figure 7. Floatability of different concentrations of Zn^{+2} ions at pH 7 using 1000 mg/L of LS and 1×10^{-3} mol/L of HOL

Table 1. Effect of temperatures on the floatability (%) of 6.5 mg/L of Zn^{+2} ions at pH 7 using 1000 mg/L of LS and 1×10^{-3} mol/L of HOL after 5 min shaking

Temperature, ºC	% F without shaking	% F with shaking, 5 min
3	90.0	99.2
5	94.0	99.9
10	95.1	99.9
30	95.9	100.0
40	97.2	99.9
60	96.3	99.7
70	96.4	99.6
80	91.1	99.5

Effect of Temperature

Studies of the influence of temperature on the flotation efficiency of Zn^{2+} ions seemed to be important from a practical viewpoint, especially in the case of hot industrial effluents. For such studies, one solution containing 6.5 mg/L Zn^{2+} ions and 1000 mg/L of LS and a second solution containing 1×10^{-3} mol/L of HOL were either heated or cooled to the same temperature using a water bath. The surfactant solution was quickly poured onto the Zn^{2+} ions solution contained within a flotation cell jacketed with 1-cm thick fiberglass insulation. The mixture was then floated using the previously described procedure. The results obtained (Table 1) indicated that the percentage removal of Zn^{2+} ions (~ 100%) was not markedly affected by raising the temperature from 3 to 80º C after shaking for 5 min. Therefore, the simple procedure presented here may find application in the removal of Zn^{2+} ions from hot industrial wastewater.

Effect of Shaking Time

The effect of manually shaking time (2-30 min) on the floatability of 6.5 mg/L of Zn^{2+} ions was investigated at pH 7 using 1000mg/L LS and 1×10^{-3} mol/L of HOL. The data obtained showed that the removal of Zn^{2+} ions is almost quantitatively (~ 100%) after shaking from 3 to 30 min. So, 5 min shaking was recommended for all experiments in this investigation.

Effect of Foreign Ions

Under the optimized conditions determined as above, the percentage removal of 6.5 mg/L of Zn^{2+} ions from a solution of pH 5 containing 1000 mg/L of LS and 1×10^{-3} mol/L of HOL was studied (with shaking for 5 min) in the presence of high concentrations of various cations and anions, usually found in some natural water samples. All cations were used as their nitrates whereas the anions were used as their sodium or potassium salts. The tolerable amounts of each ion giving a maximum error of ± 2% in the flotation efficiency are summarized in Table 2. An inspection of the data indicates that the floatability of Zn^{2+} ions was quantitative (~ 100 %) in most cases. Moreover, shaking for 5 min enhances the process. However, it should be noted that higher concentrations of Al^{3+}, Cr^{3+}, Cu^{2+} or Cd^{2+} could have harmful effect on the removal process. This may be due to competition between these cations and Zn^{2+} ions for sorption onto the active sites of LS. This problem could be overcome by increasing the amount of sorbent. Thus, the recommended procedure could be fairly employed for the removal of Zn^{2+} ions from various complex water samples.

Table 2. Effect of some selected foreign ions on the floatability (%) of 6.5 mg/L of Zn^{2+} ions at pH 5 using 1000 mg/L of LS and 1×10^{-3} mol/L of HOL after 5 min shaking

Cations	Concentration, $\times10^3$ (mg/L)	% F After 5 min shaking
Na^+	11.0	99.9
Ba^{2+}	13.8	98.4
NH_4^+	2.0	98.4
K^+	4.0	98.9
Mg^{2+}	12.5	99.4
Ca^{2+}	10.0	99.8
Cu^{2+}	3.2	99.2
Cd^{2+}	3.2	98.1
Al^{3+} or Cr^{3+}	1.4	98.2
Anions	**Concentration, $\times10^3$ (mg/L)**	**% F After 5 min shaking**
Cl^-	3.5	99.5
I^-	63.5	99.4
CO_3^{2-}	6.0	99.0
SO_4^{2-}	48	99.1
$S_2O_3^{2-}$	5.6	99.3
S^{2-}	16	99.2
$CH3COO^-$	5.5	99.0

Table 3. Recovery of Zn^{2+} ions from various natural water samples of pH 7 using 2000 mg/L of LS and 1×10^{-3} mol/L of HOL after 5 min shaking

Sample (location)	Added Zn^{2+} (mg.L^{-1})	% F
Tap water (our laboratory)	5.0	99.9
	8.0	100.0
	15.0	99.9
Nile water (Mansoura City)	5.0	99.8
	8.0	99.9
	15.0	99.7
Sea water (Gamasah)	5.0	99.7
	8.0	99.8
	15.0	99.7
Underground water (Salaka)	5.0	98.9
	8.0	99.3
	15.0	99.6
Lake water (El-Manzala)	5.0	98.1
	8.0	99.0
	15.0	99.2

IV. APPLICATION

To investigate the applicability of the recommended procedure, a series of experiments was performed to recover 5.0, 8.0 and 15.0 mg/L of Zn^{2+} ions added to aqueous and some natural water samples. The sportive-flotation experiments were carried out using 1 L of clear, filtered, uncontaminated sample solutions after adjusting their pH values to 7. The results obtained are listed in Table 3 and show that the recovery was satisfactory (~ 100 %). Moreover, the data indicated that the method could be successfully applied for the separation of Zn^{2+} ions from natural water samples containing large amounts of salt matrix under the recommended conditions.

V. CONCLUSION

Limestone (LS) was used in this study as a good sorbent for the heavy meals as zinc. Flotation technique which has advantages (compared with other separation methods) of being simple, inexpensive, less time consuming and expected to be soon incorporated as a clean technology to treat water and wastewater has been applied in this investigation. The removal of Zn^{2+} ions at pH 7, attained ~100% in the presence of LS and oleic acid as a cheap surfactant. Moreover, the recommended procedure was successfully applied to some natural water samples and was nearly free from interferences of some selected foreign ions. Moreover, the zinc ions were essentially held up by LS sorbent and would not leached out by acids owing to the solubility of the sorbent. Therefore, the metal-loaded solid waste could be solidified to an environmentally safe form used in building constructions, thereby serving the double-fold aim of water treatment and solid waste disposal.

REFERENCES

Baes, C.F and R.E. Messmer, *The Hydrolysis of Cations*, Krieger Publishing Co. Florida (1976).

Bailey, S.E., I.J. Olin, R.M. Bricka and D.D. Adrian, "A review of Potentially Low-Coast Sorbents for Heavy Metals," *Water Res.,* **33,** 2469-2479 (1999).

Bates, R.L. and J.A. Jackson, *Glossary of Geology*, 2nd Ed.; American Geological Institute: Falls Church, VA (1980).

Bradl, H.B., "Adsorption of Heavy Metal Ions on Soils and Soils Constituents," *J. Colloid Interface Sci.*, **277**, 1-18 (2004).

Ghazy, S.E., "Removal of Cadmium, Lead, Mercury, Tin, Antimony, and Arsenic from Drinking and Sea Water by Colloid Precipitate Flotation," *Sep. Sci. Technol.*, **30**, 933-947 (1995).

Ghazy, S.E., S.E. Samra, and S.M. El-Morsy, "Removal of Copper(II) from Aqueous Solutions Using Limestone Fines As the sorbent and Oleic Acid As the Surfactant," *Adsorp. Sci. Technol.,* **19**, 175-185 (2001).

Ghazy, S.E., S.E. Samra, A.M. Mahdy and S.M. El-Morsy, "Flotation Separation of Aluminum from Water Samples Using Powdered Marble Wastes and Oleic Acid," *Anal. Sci.,* **19,** 1401-1411 (2003).

Ghazy, S.E., S.E. Samra, A.M. Mahdy and S.M. El-Morsy, "Kinetic Investigation of the Removal of Aluminum from Water Samples by Adsorption onto Powdered Marble Wastes," *Sep. Sci. Technol.*, **40**, 1797-1815 (2005).

Gomez del Rio, J.A, P.J. Morando and D.S. Cicerone, "Natural Materials for Treatment of Industrial Effluents: Cmparative Study of the Retention of Cd, Zn and Co by Calcite and Hydroxyaptite. Part I: Batch Experiments," *J. Environ. Manage.,* **71,** 169-177 (2004).

Guangy, Y., and V. Thiruvenkatachari, "Heavy Metals Removal from Aqueous Solution by Fungus Mucor Rouxii," *Water res.,* **37**, 4486-4496 (2003).

Komnitsas, K., G. Bartzas and I. Paspaliarise, "Efficiency of Limestone and Red Mud Barriers: Laboratory Column Studies," *Minerals Eng.,* **17,** 183-194 (2004).

Kortonekamp, A., M. Casadevall, S.P. Faux, A.A. Jenner, R.O.J. Shayer, N. Woodbrige and P.O. Brein, "A role of Molecular Oxygen in the Formation of DNA Damage During the Reduction of the Carcinogen Chromium(VI) by Glutanioue," *Arch. Biochem. Biophys.,* **329**, 199-208 (1966).

Mandjiny, S., A.I. Zouboulis and K.I. Maties, "Removal of Cadmium from Diluted Solutions by Hydroxyapatite. Part I. Sorption Studies," *Sep. Sci. Technol.*, **30,** 2963-2978 (1995).

Nasir, M.H., R. Nadeem, K. Akhtar, M.A. Hanif and A.M. Khalid, "Efficacy of Modified Distillation Sludge of Rose (Rosa Centifolia) Petals for Lead(II) and Zinc(II) Removal from Aqueous Solutions," *J. Hazardous Materials*, **147**, 1006-1014 (2007).

Palterson, J.W., "Industrial Waste Reduction," *Environ. Sci. Technol,* **23**, 1032-1038 (1989).

Puranike, P.R. and K.M. Pakniker, "Biosorption of Lead, Cadmium and Zinc by Citrobacter Strain MCM B-181: Characterization Studies," *Biotechnol Progress*, **15**, 228-237 (1999).

Rubio, J., M.L. Souza and R.W. Smith. "Overview of Flotation as a Waste water Treatment Technique," *Minerals Eng*, **15**, 139-155 (2002).

Somasundran, P. and G.E. Agar, "Zero point of charge of calcite," *J. Colloid Interface Sci.*, **24**, 433-440 (1967).

Stoica, L., M. Dinculescu and C.G. Plapcianu, "Mn(II) Recovery from Aqueous System by Flotation," *Water Res.*, **32**, 3021-3030 (1998).

Received: August 2, 2009.
Accepted: April 28, 2010.
Recommended by Subject Editor Ana L. Cukierman.